

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-356686

(43)Date of publication of application : 13.12.2002

(51)Int.Cl. C10L 3/06

C07B 61/00

C07B 63/02

C07C 5/00

C07C 7/20

C07C 9/04

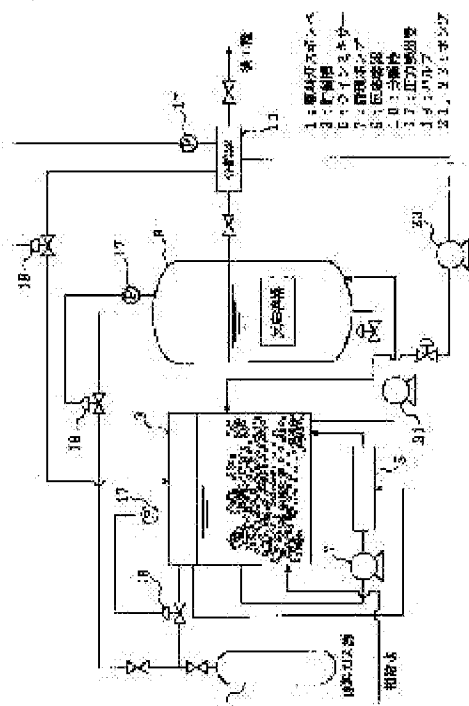
(21)Application number : 2001-162951

(71)Applicant : NKK CORP

(22)Date of filing : 30.05.2001

(72)Inventor : IDA HIROYUKI  
KODA KAZUO

## (54) METHOD AND APPARATUS FOR PRODUCING GAS HYDRATE



### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a method and an apparatus for producing a gas hydrate that is efficiently produced by effectively diffusing gas into water.

**SOLUTION:** The method for producing the gas hydrate consists of a reacting step water with the gas as raw materials, a fine bubble formation step of mixing the gas with the water, a dissolution acceleration step of feeding the water containing the formed fine bubbles into a storage tank the gas hydrate formation step of enabling the water promoted in gas dissolution to react at a specified temperature under a specified pressure are provided.

---

## CLAIMS

---

5 [Claim(s)]

[Claim 1] A method characterized by comprising the following of making raw material water and material gas react, and manufacturing gas-hydrate.

10 A fine bubble generation process of making material gas mixing in raw material underwater, and generating a fine bubble.

A dissolution acceleration process which supplies raw material water in which a fine bubble was generated to a depot in which raw material water was stored, and promotes the dissolution in raw material water of material gas.

15 A gas-hydrate generation process of making raw material water by which dissolution promotion was carried out reacting at a predetermined pressure and temperature, and generating gas-hydrate.

[Claim 2] The gas-hydrate manufacturing method according to claim 1 having a circulating process which repeats said fine bubble generation process and said dissolution acceleration process using raw material water and non-solution gas in said depot.

25 [Claim 3] The gas-hydrate manufacturing method according to claim 1 or 2 provided with a cooling process which cools temperature of said depot to gas-hydrate generation temperature in a pressure of the depot, or near any of the freezing point, or near [ high ] the temperature.

[Claim 4] The gas-hydrate manufacturing method according to any one of claims 1 to 3 cooling a gas-hydrate generation process pouring raw material water by which dissolution promotion was carried out on a coil way.

30 [Claim 5] A device which makes raw material water and material gas react, and manufactures gas-hydrate, comprising:

A line mixer which mixes raw material water and material gas in the middle of a line, and generates a fine bubble of material gas.

A depot which stores raw material water in which a fine bubble was generated.

35 A gas-hydrate generating device which makes raw material water by which dissolution promotion was carried out react at a predetermined pressure and temperature with a depot, and generates gas-hydrate.

40 [Claim 6] The gas-hydrate manufacturing installation according to claim 5 provided with a circulating route which supplies raw material water and non-solution gas in said depot to said line mixer.

45 [Claim 7] The gas-hydrate manufacturing installation according to claim 5 or 6 provided with a cooling method which cools temperature of said depot to gas-hydrate generation temperature in a pressure of the depot, or near any of the freezing point, or near [ high ] the temperature.

[Claim 8]The gas-hydrate manufacturing installation according to any one of claims 5 to 6, wherein a gas-hydrate generating device consists of a coil way cooled while pouring raw material water by which dissolution promotion was carried out.

5

---

## DETAILED DESCRIPTION

---

10 [Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method and device of gas-hydrate which, for example, make material gas and water, such as natural gas, react, and  
15 manufacture gas-hydrate.

[0002]

[Description of the Prior Art]Gas-hydrate is a substance of the shape of ice which involves gas molecules, such as natural gas and carbon dioxide, at high concentration inside the basket-like  
20 structure which a water molecule constitutes. The gas-hydrate can involve a lot of gases per unit volume, and since it compares with liquefied natural gas and can moreover store and convey in the bottom relatively high temperature of atmospheric pressure, transportation of natural gas etc. and the application to storage attract attention. For this reason, although the examination about use of the gas-hydrate which exists naturally was a center conventionally, the trial which  
25 manufactures this industrially in recent years paying attention to this character is performed.

[0003]If the gas-hydrate manufacturing process currently performed conventionally is outlined, the temperature of a gas and water and a pressure will be held in the hydrate generation range shown by an equilibrium curve in material gas and water, such as natural gas, and gas-hydrate  
30 will be generated by contacting and dissolving both. Separation drying is carried out from unreacted gas and raw material water, each processing of freezing, molding, etc. is performed further, and what is called generated sherbet form gas-hydrate is stored in a storage facility. And it is taken out and conveyed from a storage facility if needed.

35 [0004]By the way, in the manufacturing process of gas-hydrate, it is considered as the important factor which carries out order of the generation rate of gas-hydrate, and the diffusion dissolution rate to the water of gas is mentioned.

[0005]It is considered as the art of raising the dissolution rate to the water of gas and  
40 manufacturing gas-hydrate efficiently, and there are the manufacturing installation of natural gas-hydrate and the invention of a manufacturing method which were indicated by JP,2001-10985,A shown, for example in drawing 5. The porous plate 55 with which the invention of the gazette divides the inside of the resisting pressure container 51 and the resisting pressure container 51 to the gas space 56 and the gas-liquid contact space 52, The coil evaporator 53  
45 arranged in the gas-liquid contact space 52 at two or more steps, The freezer 58 which supplies a refrigerant to this, and the storage tank 62 of gas-hydrate connected with the exit of the gas-

liquid contact space 52 via the buffer tank 59, The raw material water supply piping 61 which supplies the water of the pars basilaris ossis occipitalis to the pars basilaris ossis occipitalis in the gas-liquid contact space 52, Gas-hydrate manufacturing unit A which has the material gas charging line 57 which supplies natural gas to the gas space 56, Two or more B and D are  
5 connected according to the constituent gas of natural gas, the gas draw pipe 70 is connected to the upper space part of each storage tank 62, and this is connected with the resurgent gas mixer 66 of a slipstream.

[0006]

10 [Problem(s) to be Solved by the Invention]However, there are the following problems in the above-mentioned conventional technology. In the above-mentioned conventional technology, in order to promote the underwater gas diffusion dissolution, the method of enlarging the touch area of water and gas is adopted by generating the fine bubble of gas with the porous plate 55. However, in the method of introducing air bubbles via such a porous plate 55, the cell diameter  
15 which can be generated can seldom expect the gas dissolution facilitatory effect by gas-liquid interface area expansion so small. The space for on the other hand installing the porous plate 55 which has the area more than fixed is required, Since it is necessary to also secure the gas-liquid contact space 52 for contacting vapor-liquid within the resisting pressure container 51 more than fixed, it is necessary to enlarge capacity of the resisting pressure container 51, and there is a  
20 problem that equipment becomes large. A hydrate adheres to the porous plate 55 and it grows up, and in being the worst, there is a possibility that a hole may be blockaded.

[0007]It is made in order that this invention may solve this technical problem, and it aims at obtaining the manufacturing method and device of gas-hydrate which manufacture gas-hydrate  
25 efficiently by performing underwater gas diffusion effectively.

[0008]

[Means for Solving the Problem]A manufacturing method of gas-hydrate of this invention is characterized by that what makes raw material water and material gas react, and manufactures  
30 gas-hydrate comprises:

A fine bubble generation process of making material gas mixing in raw material underwater, and generating a fine bubble.

A dissolution acceleration process which supplies raw material water in which a fine bubble was generated to a depot in which raw material water was stored, and promotes the dissolution in raw  
35 material water of material gas.

A gas-hydrate generation process of making raw material water by which dissolution promotion was carried out reacting at a predetermined pressure and temperature, and generating gas-hydrate.

40 [0009]It has a circulating process which repeats a fine bubble generation process and said dissolution acceleration process using raw material water and non-solution gas in a depot.

[0010]It has a cooling process which cools temperature of a depot to gas-hydrate generation temperature in a pressure of the depot, or near any of the freezing point, or near [ high ] the  
45 temperature.

[0011]A gas-hydrate generation process is cooled pouring raw material water by which dissolution promotion was carried out on a coil way.

[0012]A gas-hydrate manufacturing installation of this invention is characterized by that what makes raw material water and material gas react, and manufactures gas-hydrate comprises:  
A line mixer which mixes raw material water and material gas in the middle of a line, and generates a fine bubble of material gas.

A depot which stores raw material water in which a fine bubble was generated.

A gas-hydrate generating device which makes raw material water by which dissolution promotion was carried out react at a predetermined pressure and temperature with a depot, and generates gas-hydrate.

[0013]It has a circulating route which supplies raw material water and non-solution gas in a depot to said line mixer.

[0014]It has a cooling method which cools temperature of a depot to gas-hydrate generation temperature in a pressure of the depot, or near any of the freezing point, or near [ high ] the temperature.

[0015]A gas-hydrate generating device consists of a coil way cooled while pouring raw material water by which dissolution promotion was carried out.

[0016]

[Embodiment of the Invention]Embodiment 1. drawing 4 is an explanatory view of the outline of the gas-hydrate manufacturing process of the 1 embodiment of this invention, and shows the thing using natural gas as material gas. First, the outline of a gas-hydrate manufacturing process is explained based on drawing 4. Natural gas is cooled by 1-10 \*\*, and a heavy ingredient is separated as condensate (S1). On the other hand, it is cooled by 1-10 \*\* (S2), water also reacts in the state where this cooling water and natural gas are 1-10 \*\* and 50 atmospheres, and gas-hydrate is generated (S3). The water and the unconverted gas which separation dehydrating treatment of the gas-hydrate of the generated slurry form was carried out, were used as highly concentrated slurry or a solid, and were separated (S4) and here are again returned to a reaction process (S3).

[0017]Freezing treatment of the gas-hydrate by which separation dehydrating treatment was carried out is carried out at about [ -15 \*\* ] temperature (S5). By freezing the moisture adhering to the surface of the gas-hydrate by which separation dehydrating treatment was carried out by S4, and making icy husks, this freezing treatment is for attaining stabilization of gas-hydrate.

Decompression treatment decompressed from 50 atmospheres to atmospheric pressure is performed after freezing treatment (S6). Then, shaping processing of the gas-hydrate by which freezing treatment was carried out is carried out at a pellet type (S7), it is stored in storage facilities, such as a silo (S8), shipping processing is carried out with shipping equipment of a band conveyor etc. according to a demand, and a long haul is presented by transport apparatus, such as (S9) and a transport ship (S10). Although the above is an outline of a gas-hydrate manufacturing process, in the process (S3) of generating the gas-hydrate of slurry form, this embodiment devises from water and natural gas in the above-mentioned process. Hereafter, this

point is explained in detail.

[0018]Drawing 1 is a distribution diagram showing the main configuration equipment of the 1 embodiment of this invention. First, the configuration equipment of this embodiment is explained based on drawing 1. The gas-hydrate manufacturing installation of this embodiment, Store the source 1 of material gas and raw material water which store material gas, such as natural gas, with specified pressure, and. The raw material water of the depot 3 and the depot 3 which has the function to promote the dissolution in the raw material water of material gas is supplied to the below-mentioned line mixer 5. The line mixer 5 which mixes the raw material water supplied from the circulating pump 7 which performs a raw material hydrologic cycle, and the circulating pump 7, and the non-solution gas in the depot 3, and generates the fine bubble of material gas, and the raw material water by which dissolution promotion was carried out with the depot 3 A predetermined pressure, It has the eliminator 10 which separates the gas-hydrate, the unconverted gas, and raw material water which were generated with the reaction vessel 9 which makes it react at temperature and generates gas-hydrate, and the reaction vessel 9. And each valve 19 which each configuration equipment was connected by piping shown as the solid line which attached the figure Nakaya seal, and the pressure sensor 17 was installed in the key point, and was installed in the piping line by the signal of this pressure sensor 17 is controlled, and it is constituted so that the pressure of the piping line concerned and a flow may be adjusted.

[0019]The composition of main things is explained still in detail among each of above-mentioned configuration equipment. As shown in drawing 2 (it quotes from the 7th page of the SEIKA CORP. "OHR line mixer" catalog), the line mixer 5 of this embodiment, An outlet side consists of the tube-like object 11 of the shape of two step which became a byway by a major diameter, and the entrance side has the wing object 13 called a guide vane into the major diameter 11a of this tube-like object 11, and has the collision body 15 of the shape of two or more mushroom prolonged in the center from the inner skin of a pipe in the narrow diameter portion 11b of that point. In such a line mixer 5, the raw material water supplied to the line mixer 55 by the circulating pump 7 serves as a turning stream with the wing object 13, It is pushed aside outside by a violent centrifugal force, and it is stirred still more intensely with the mushroom-like collision body 15, and material gas is involved in into it, it is broken by the overly detailed cellular group, and raw material water and material gas are mixed. By this, the touch area of material gas and raw material water becomes large, and material gas melts into raw material water efficiently.

[0020]The depot 3 has output port of non-solution gas in the upper part, and has an intake of the raw material water having contained the fine bubble of the material gas breathed out by the lower part from the line mixer 5. And the depot 3 is provided with the cooling method cooled to the gas-hydrate generation temperature in the pressure of the depot 3, or near any of the freezing point, or near [ high ] the temperature. As an example of this cooling method, it may be a thing of the mode which cools the circumference of the depot 3, and may be a thing of the mode which cools a raw material hydrologic cycle course. Since the thing of the mode which cools a circulating route should just cool the pipeline which constitutes a circulating route, it can attain the simplification of a device.

[0021]Although the eliminator 10 separates gas-hydrate, a unconverted gas, and raw material water, it can consider a decanter, a cyclone, the centrifuge 10, a belting press, screw concentration and a dehydrator, a rotation dryer, etc. as an example of the eliminator 10.

5 [0022]Next, the manufacturing process which manufactures gas-hydrate with the device of this embodiment constituted as mentioned above is explained. Material gas is supplied to the depot 3 in which raw material water was stored. Then, a part of material gas melts into raw material water, and the material gas which is not dissolved [ other ] is supplied to the line mixer 5. The circulating pump 7 is worked and the raw material water in the depot 3 is supplied to the line mixer 5. The material gas supplied to the line mixer 5 and raw material water are mixed with violent vigor by the mechanism mentioned above. At this time, material gas serves as a fine bubble, and is mixed into raw material water, and the dissolution of material gas is considerably promoted also at this process. By the line mixer 5, the raw material water in which the fine bubble was generated is returned to the depot 3 from the lower part of the depot 3, it stagnates temporarily within the depot 3, and the dissolution in the raw material water of material gas is promoted.

20 [0023]Pressure up of the raw material water in which material gas melted from the lower part of the depot 3 is carried out to a predetermined pressure with the pump 21, it is sent to the reaction vessel 9, it is cooled by predetermined temperature, and gas-hydrate is generated. And the gas-hydrate generated here is sent to the eliminator 10, and is divided into gas-hydrate, a unconverted gas, and raw material water. The separated raw material water is again returned to the depot 3 with the pump 23 with the unreacted raw material water in the reaction vessel 9. Though the raw material water with which gas-hydrate generation was not presented is returned, since a constant rate of raw material water is consumed, in order to compensate this, raw material water is supplied to the depot 3 from the makeup water line shown in drawing 1. The unreacted material gas separated with the eliminator 10 as well as the case of raw material water is again returned to the depot 3 with the unreacted material gas in the reaction vessel 9. On the other hand, the generated gas-hydrate is taken out from the eliminator 10, and is sent to a tail end process (process after S5 in drawing 4).

35 [0024]As mentioned above, according to this embodiment, the line mixer 5 which consists of the barrel 11 performs continuously the dissolution in the raw material water of material gas, and. Since it was made to stagnate temporarily with the depot 3 and promotion of the dissolution to the raw material water of material gas was aimed at, material gas can raise the production efficiency of penetration and gas-hydrate to raw material water efficiently.

40 [0025]Since it has cooled to near the reaction temperature in the depot 3 or the raw material hydrologic cycle course, cooling with the reaction vessel 9 can be simplified and the simplification of a device and miniaturization are attained.

45 [0026]Embodiment 2. drawing 3 is an explanatory view of other embodiments of this invention, and has given the same numerals to drawing 1 and identical parts which showed Embodiment 1. In this embodiment, it replaces with the reaction vessel 9 of Embodiment 1, and the coil way 25 is used. The coil way 25 consists of a crooked pipe of the singular number or plurality, and cools the peripheral surface of this pipe with the chiller 27. thus, since cooling from the pipe

circumference can be efficiently performed by having used the coil way 25, it becomes unnecessary to cool material gas and raw material water directly with a cooling coil etc. like a conventional example, and the composition of a device is simple -- and it is miniaturizable. And since cooling efficiency is good, reaction velocity is quick and the production efficiency of gas-hydrate can be raised.

[0027]It is because that such a coil way 25 can be used can perform beforehand mixing and the dissolution of material gas and raw material water with the line mixer 5 and the depot 3 and it can consider an equipment configuration focusing on cooling on the coil way 25. Namely, since material gas, mixing and the dissolution of raw material water, and reaction cooling were performed within the tub-like resisting pressure container in the conventional example, In this embodiment to the ability to have not cooled only from the circumference of the reaction vessel by the space which had fixed breadth in mixing and the dissolution being needed, Since material gas, mixing and the dissolution of raw material water, and reaction cooling were separated, in a reaction process, it can think focusing on cooling and cooling with simple composition is attained like the above-mentioned example.

[0028]Since it was made to perform the reaction of raw material water and material gas in this embodiment, moving a pipeline, in this gas-hydrate generation process. The mechanism in which all the things (the gas-hydrate, the unconverted gas, raw material water which were generated) take out only the gas-hydrate which the eliminator 10 will once be sent and was generated like a conventional example is unnecessary, and the composition of a device can be simplified. However, since the eliminator 10 is sent without returning a unconverted gas with the reaction vessel 9 like Embodiment 1, Since the danger that a unconverted gas will flow into a raw material water return line is high, in order to avoid this, by detecting with the water level - the level indicator 29 in the eliminator 10, and adjusting the valve 31, it controls so that the water level in the eliminator 10 becomes more than a constant level, and the sealing water effect is given to raw material water.

[0029]Although it does not show clearly about the temperature in each process, and a pressure in particular in the above-mentioned explanation, what was shown by drawing 4 as an example can be mentioned. However, an optimum value is chosen by the conditions of versatility [ pressure / the temperature in each process, and ]. In the above-mentioned embodiment, although the natural gas which uses methane as the main ingredients as material gas was explained, there are ethane, propane, butane, krypton, a xenon, carbon dioxide, etc. as other examples.

[0030]As other examples of the line mixer 5, May be the so-called thing of the venturi tube method which attracts material gas and is mixed by making the middle of a tube-like object thin and generating negative pressure, and, It is or like the revolution type fine bubble generator indicated by what carries out vapor-liquid mixing using the turning stream in a cone or a truncated cone form container, for example, JP,2000-447,A. In short, what is on a line, mixes vapor-liquid and can generate the fine bubble of material gas is widely included in the line mixer 5 in this specification. Although the singular number or two or more crookedness pipes were shown as an example of the coil way 25 in the above-mentioned embodiment, it may constitute from two or more branched straight pipes.



[0031]

[Effect of the Invention]The fine bubble generation process of making material gas mixing in raw material underwater, and generating a fine bubble in this invention as explained above, The dissolution acceleration process which supplies the raw material water in which the fine bubble was generated to the depot in which raw material water was stored, and promotes the dissolution in the raw material water of material gas, By having had the gas-hydrate generation process of making the raw material water by which dissolution promotion was carried out reacting at a predetermined pressure and temperature, and generating gas-hydrate, the underwater gas diffusion dissolution can be performed effectively and gas-hydrate can be manufactured efficiently.

---

## TECHNICAL FIELD

---

[Field of the Invention]This invention relates to the manufacturing method and device of gas-hydrate which, for example, make material gas and water, such as natural gas, react, and manufacture gas-hydrate.

---

## PRIOR ART

---

[Description of the Prior Art]Gas-hydrate is a substance of the shape of ice which involves gas molecules, such as natural gas and carbon dioxide, at high concentration inside the basket-like structure which a water molecule constitutes. The gas-hydrate can involve a lot of gases per unit volume, and since it compares with liquefied natural gas and can moreover store and convey in the bottom relatively high temperature of atmospheric pressure, transportation of natural gas etc. and the application to storage attract attention. For this reason, although the examination about use of the gas-hydrate which exists naturally was a center conventionally, the trial which manufactures this industrially in recent years paying attention to this character is performed.

[0003]If the gas-hydrate manufacturing process currently performed conventionally is outlined, the temperature of a gas and water and a pressure will be held in the hydrate generation range shown by an equilibrium curve in material gas and water, such as natural gas, and gas-hydrate will be generated by contacting and dissolving both. Separation drying is carried out from unreacted gas and raw material water, each processing of freezing, molding, etc. is performed further, and what is called generated sherbet form gas-hydrate is stored in a storage facility. And it is taken out and conveyed from a storage facility if needed.

[0004]By the way, in the manufacturing process of gas-hydrate, it is considered as the important factor which carries out order of the generation rate of gas-hydrate, and the diffusion dissolution rate to the water of gas is mentioned.

[0005]It is considered as the art of raising the dissolution rate to the water of gas and manufacturing gas-hydrate efficiently, and there are the manufacturing installation of natural gas-hydrate and the invention of a manufacturing method which were indicated by JP,2001-10985,A shown, for example in drawing 5. The porous plate 55 with which the invention of the  
5 gazette divides the inside of the resisting pressure container 51 and the resisting pressure container 51 to the gas space 56 and the gas-liquid contact space 52, The coil evaporator 53 arranged in the gas-liquid contact space 52 at two or more steps, The freezer 58 which supplies a refrigerant to this, and the storage tank 62 of gas-hydrate connected with the exit of the gas-liquid contact space 52 via the buffer tank 59, The raw material water supply piping 61 which  
10 supplies the water of the pars basilaris ossis occipitalis to the pars basilaris ossis occipitalis in the gas-liquid contact space 52, Gas-hydrate manufacturing unit A which has the material gas charging line 57 which supplies natural gas to the gas space 56, Two or more B and D are connected according to the constituent gas of natural gas, the gas draw pipe 70 is connected to the upper space part of each storage tank 62, and this is connected with the resurgent gas mixer  
15 66 of a slipstream.

---

## EFFECT OF THE INVENTION

---

[Effect of the Invention]The fine bubble generation process of making material gas mixing in raw material underwater, and generating a fine bubble in this invention as explained above, It had the dissolution acceleration process which supplies the raw material water in which the fine  
25 bubble was generated to the depot in which raw material water was stored, and promotes the dissolution in the raw material water of material gas, and the gas-hydrate generation process of making the raw material water by which dissolution promotion was carried out reacting at a predetermined pressure and temperature, and generating gas-hydrate.  
Therefore, the underwater gas diffusion dissolution can be performed effectively and gas-hydrate  
30 can be manufactured efficiently.

---

## TECHNICAL PROBLEM

---

[Problem(s) to be Solved by the Invention]However, there are the following problems in the above-mentioned conventional technology. In the above-mentioned conventional technology, in order to promote the underwater gas diffusion dissolution, the method of enlarging the touch area  
40 of water and gas is adopted by generating the fine bubble of gas with the porous plate 55. However, in the method of introducing air bubbles via such a porous plate 55, the cell diameter which can be generated can seldom expect the gas dissolution facilitatory effect by gas-liquid interface area expansion so small. The space for on the other hand installing the porous plate 55 which has the area more than fixed is required, Since it is necessary to also secure the gas-liquid  
45 contact space 52 for contacting vapor-liquid within the resisting pressure container 51 more than fixed, it is necessary to enlarge capacity of the resisting pressure container 51, and there is a

problem that equipment becomes large. A hydrate adheres to the porous plate 55 and it grows up, and in being the worst, there is a possibility that a hole may be blockaded.

5 [0007]It is made in order that this invention may solve this technical problem, and it aims at obtaining the manufacturing method and device of gas-hydrate which manufacture gas-hydrate efficiently by performing underwater gas diffusion effectively.

---

10 MEANS

---

[Means for Solving the Problem]A manufacturing method of gas-hydrate of this invention is characterized by that what makes raw material water and material gas react, and manufactures  
15 gas-hydrate comprises:

A fine bubble generation process of making material gas mixing in raw material underwater, and generating a fine bubble.

20 A dissolution acceleration process which supplies raw material water in which a fine bubble was generated to a depot in which raw material water was stored, and promotes the dissolution in raw material water of material gas.

A gas-hydrate generation process of making raw material water by which dissolution promotion was carried out reacting at a predetermined pressure and temperature, and generating gas-hydrate.

25 [0009]It has a circulating process which repeats a fine bubble generation process and said dissolution acceleration process using raw material water and non-solution gas in a depot.

[0010]It has a cooling process which cools temperature of a depot to gas-hydrate generation temperature in a pressure of the depot, or near any of the freezing point, or near [ high ] the  
30 temperature.

[0011]A gas-hydrate generation process is cooled pouring raw material water by which dissolution promotion was carried out on a coil way.

35 [0012]A gas-hydrate manufacturing installation of this invention is characterized by that what makes raw material water and material gas react, and manufactures gas-hydrate comprises:  
A line mixer which mixes raw material water and material gas in the middle of a line, and generates a fine bubble of material gas.

A depot which stores raw material water in which a fine bubble was generated.

40 A gas-hydrate generating device which makes raw material water by which dissolution promotion was carried out react at a predetermined pressure and temperature with a depot, and generates gas-hydrate.

[0013]It has a circulating route which supplies raw material water and non-solution gas in a  
45 depot to said line mixer.

[0014]It has a cooling method which cools temperature of a depot to gas-hydrate generation temperature in a pressure of the depot, or near any of the freezing point, or near [ high ] the temperature.

- 5 [0015]A gas-hydrate generating device consists of a coil way cooled while pouring raw material water by which dissolution promotion was carried out.

[0016]

- 10 [Embodiment of the Invention]Embodiment 1. drawing 4 is an explanatory view of the outline of the gas-hydrate manufacturing process of the 1 embodiment of this invention, and shows the thing using natural gas as material gas. First, the outline of a gas-hydrate manufacturing process is explained based on drawing 4. Natural gas is cooled by 1-10 \*\*, and a heavy ingredient is separated as condensate (S1). On the other hand, it is cooled by 1-10 \*\* (S2), water also reacts in the state where this cooling water and natural gas are 1-10 \*\* and 50 atmospheres, and gas-hydrate is generated (S3). The water and the unconverted gas which separation dehydrating treatment of the gas-hydrate of the generated slurry form was carried out, were used as highly concentrated slurry or a solid, and were separated (S4) and here are again returned to a reaction process (S3).

- 20 [0017]Freezing treatment of the gas-hydrate by which separation dehydrating treatment was carried out is carried out at about [ -15 \*\* ] temperature (S5). By freezing the moisture adhering to the surface of the gas-hydrate by which separation dehydrating treatment was carried out by S4, and making icy husks, this freezing treatment is for attaining stabilization of gas-hydrate. Decompression treatment decompressed from 50 atmospheres to atmospheric pressure is performed after freezing treatment (S6). Then, shaping processing of the gas-hydrate by which freezing treatment was carried out is carried out at a pellet type (S7), it is stored in storage facilities, such as a silo (S8), shipping processing is carried out with shipping equipment of a band conveyor etc. according to a demand, and a long haul is presented by transport apparatus, such as (S9) and a transport ship (S10). Although the above is an outline of a gas-hydrate manufacturing process, in the process (S3) of generating the gas-hydrate of slurry form, this embodiment devises from water and natural gas in the above-mentioned process. Hereafter, this point is explained in detail.

- 35 [0018]Drawing 1 is a distribution diagram showing the main configuration equipment of the 1 embodiment of this invention. First, the configuration equipment of this embodiment is explained based on drawing 1. The gas-hydrate manufacturing installation of this embodiment, Store the source 1 of material gas and raw material water which store material gas, such as natural gas, with specified pressure, and. The raw material water of the depot 3 and the depot 3 which has the function to promote the dissolution in the raw material water of material gas is supplied to the below-mentioned line mixer 5. The line mixer 5 which mixes the raw material water supplied from the circulating pump 7 which performs a raw material hydrologic cycle, and the circulating pump 7, and the non-solution gas in the depot 3, and generates the fine bubble of material gas, and the raw material water by which dissolution promotion was carried out with the depot 3 A predetermined pressure, It has the eliminator 10 which separates the gas-hydrate, the unconverted gas, and raw material water which were generated with the reaction vessel 9 which makes it react at temperature and generates gas-hydrate, and the reaction vessel 9. And each

valve 19 which each configuration equipment was connected by piping shown as the solid line which attached the figure Nakaya seal, and the pressure sensor 17 was installed in the key point, and was installed in the piping line by the signal of this pressure sensor 17 is controlled, and it is constituted so that the pressure of the piping line concerned and a flow may be adjusted.

[0019]The composition of main things is explained still in detail among each of above-mentioned configuration equipment. As shown in drawing 2 (it quotes from the 7th page of the SEIKA CORP. "OHR line mixer" catalog), the line mixer 5 of this embodiment, An outlet side consists of the tube-like object 11 of the shape of two step which became a byway by a major diameter, and the entrance side has the wing object 13 called a guide vane into the major diameter 11a of this tube-like object 11, and has the collision body 15 of the shape of two or more mushroom prolonged in the center from the inner skin of a pipe in the narrow diameter portion 11b of that point. In such a line mixer 5, the raw material water supplied to the line mixer 55 by the circulating pump 7 serves as a turning stream with the wing object 13, It is pushed aside outside by a violent centrifugal force, and it is stirred still more intensely with the mushroom-like collision body 15, and material gas is involved in into it, it is broken by the overly detailed cellular group, and raw material water and material gas are mixed. By this, the touch area of material gas and raw material water becomes large, and material gas melts into raw material water efficiently.

[0020]The depot 3 has output port of non-solution gas in the upper part, and has an intake of the raw material water having contained the fine bubble of the material gas breathed out by the lower part from the line mixer 5. And the depot 3 is provided with the cooling method cooled to the gas-hydrate generation temperature in the pressure of the depot 3, or near any of the freezing point, or near [ high ] the temperature. As an example of this cooling method, it may be a thing of the mode which cools the circumference of the depot 3, and may be a thing of the mode which cools a raw material hydrologic cycle course. Since the thing of the mode which cools a circulating route should just cool the pipeline which constitutes a circulating route, it can attain the simplification of a device.

[0021]Although the eliminator 10 separates gas-hydrate, a unconverted gas, and raw material water, it can consider a decanter, a cyclone, the centrifuge 10, a belting press, screw concentration and a dehydrator, a rotation dryer, etc. as an example of the eliminator 10.

[0022]Next, the manufacturing process which manufactures gas-hydrate with the device of this embodiment constituted as mentioned above is explained. Material gas is supplied to the depot 3 in which raw material water was stored. Then, a part of material gas melts into raw material water, and the material gas which is not dissolved [ other ] is supplied to the line mixer 5. The circulating pump 7 is worked and the raw material water in the depot 3 is supplied to the line mixer 5. The material gas supplied to the line mixer 5 and raw material water are mixed with violent vigor by the mechanism mentioned above. At this time, material gas serves as a fine bubble, and is mixed into raw material water, and the dissolution of material gas is considerably promoted also at this process. By the line mixer 5, the raw material water in which the fine bubble was generated is returned to the depot 3 from the lower part of the depot 3, it stagnates temporarily within the depot 3, and the dissolution in the raw material water of material gas is

promoted.

[0023]Pressure up of the raw material water in which material gas melted from the lower part of the depot 3 is carried out to a predetermined pressure with the pump 21, it is sent to the reaction vessel 9, it is cooled by predetermined temperature, and gas-hydrate is generated. And the gas-hydrate generated here is sent to the eliminator 10, and is divided into gas-hydrate, a unconverted gas, and raw material water. The separated raw material water is again returned to the depot 3 with the pump 23 with the unreacted raw material water in the reaction vessel 9. Though the raw material water with which gas-hydrate generation was not presented is returned, since a constant rate of raw material water is consumed, in order to compensate this, raw material water is supplied to the depot 3 from the makeup water line shown in drawing 1. The unreacted material gas separated with the eliminator 10 as well as the case of raw material water is again returned to the depot 3 with the unreacted material gas in the reaction vessel 9. On the other hand, the generated gas-hydrate is taken out from the eliminator 10, and is sent to a tail end process (process after S5 in drawing 4).

[0024]As mentioned above, according to this embodiment, the line mixer 5 which consists of the barrel 11 performs continuously the dissolution in the raw material water of material gas, and. Since it was made to stagnate temporarily with the depot 3 and promotion of the dissolution to the raw material water of material gas was aimed at, material gas can raise the production efficiency of penetration and gas-hydrate to raw material water efficiently.

[0025]Since it has cooled to near the reaction temperature in the depot 3 or the raw material hydrologic cycle course, cooling with the reaction vessel 9 can be simplified and the simplification of a device and miniaturization are attained.

[0026]Embodiment 2. drawing 3 is an explanatory view of other embodiments of this invention, and has given the same numerals to drawing 1 and identical parts which showed Embodiment 1. In this embodiment, it replaces with the reaction vessel 9 of Embodiment 1, and the coil way 25 is used. The coil way 25 consists of a crooked pipe of the singular number or plurality, and cools the peripheral surface of this pipe with the chiller 27. thus, since cooling from the pipe circumference can be efficiently performed by having used the coil way 25, it becomes unnecessary to cool material gas and raw material water directly with a cooling coil etc. like a conventional example, and the composition of a device is simple -- and it is miniaturizable. And since cooling efficiency is good, reaction velocity is quick and the production efficiency of gas-hydrate can be raised.

[0027]It is because that such a coil way 25 can be used can perform beforehand mixing and the dissolution of material gas and raw material water with the line mixer 5 and the depot 3 and it can consider an equipment configuration focusing on cooling on the coil way 25. Namely, since material gas, mixing and the dissolution of raw material water, and reaction cooling were performed within the tub-like resisting pressure container in the conventional example, In this embodiment to the ability to have not cooled only from the circumference of the reaction vessel by the space which had fixed breadth in mixing and the dissolution being needed, Since material gas, mixing and the dissolution of raw material water, and reaction cooling were separated, in a reaction process, it can think focusing on cooling and cooling with simple composition is

attained like the above-mentioned example.

[0028] Since it was made to perform the reaction of raw material water and material gas in this embodiment, moving a pipeline, in this gas-hydrate generation process. The mechanism in which all the things (the gas-hydrate, the unconverted gas, raw material water which were generated) take out only the gas-hydrate which the eliminator 10 will once be sent and was generated like a conventional example is unnecessary, and the composition of a device can be simplified. However, since the eliminator 10 is sent without returning a unconverted gas with the reaction vessel 9 like Embodiment 1, Since the danger that a unconverted gas will flow into a raw material water return line is high, in order to avoid this, by detecting with the water level - the level indicator 29 in the eliminator 10, and adjusting the valve 31, it controls so that the water level in the eliminator 10 becomes more than a constant level, and the sealing water effect is given to raw material water.

[0029] Although it does not show clearly about the temperature in each process, and a pressure in particular in the above-mentioned explanation, what was shown by drawing 4 as an example can be mentioned. However, an optimum value is chosen by the conditions of versatility [ pressure / the temperature in each process, and ]. In the above-mentioned embodiment, although the natural gas which uses methane as the main ingredients as material gas was explained, there are ethane, propane, butane, krypton, a xenon, carbon dioxide, etc. as other examples.

[0030] As other examples of the line mixer 5, May be the so-called thing of the venturi tube method which attracts material gas and is mixed by making the middle of a tube-like object thin and generating negative pressure, and, It is or like the revolution type fine bubble generator indicated by what carries out vapor-liquid mixing using the turning stream in a cone or a truncated cone form container, for example, JP,2000-447,A. In short, what is on a line, mixes vapor-liquid and can generate the fine bubble of material gas is widely included in the line mixer 5 in this specification. Although the singular number or two or more crookedness pipes were shown as an example of the coil way 25 in the above-mentioned embodiment, it may constitute from two or more branched straight pipes.

---

## DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] It is a distribution diagram showing the main configuration equipment of the 1 embodiment of this invention.

[Drawing 2] It is an explanatory view of the line mixer 5 of the 1 embodiment of this invention.

[Drawing 3] It is a distribution diagram showing the main configuration equipment of other modes of other embodiments of this invention.

[Drawing 4] It is an explanatory view of the gas-hydrate manufacturing process of this invention.

[Drawing 5] It is an explanatory view of conventional technology.

5 [Description of Notations]

1 The source of material gas

3 Depot

5 Line mixer

7 Circulating pump

10 9 Reaction vessel

10 Eliminator

17 Pressure sensor

19 Valve

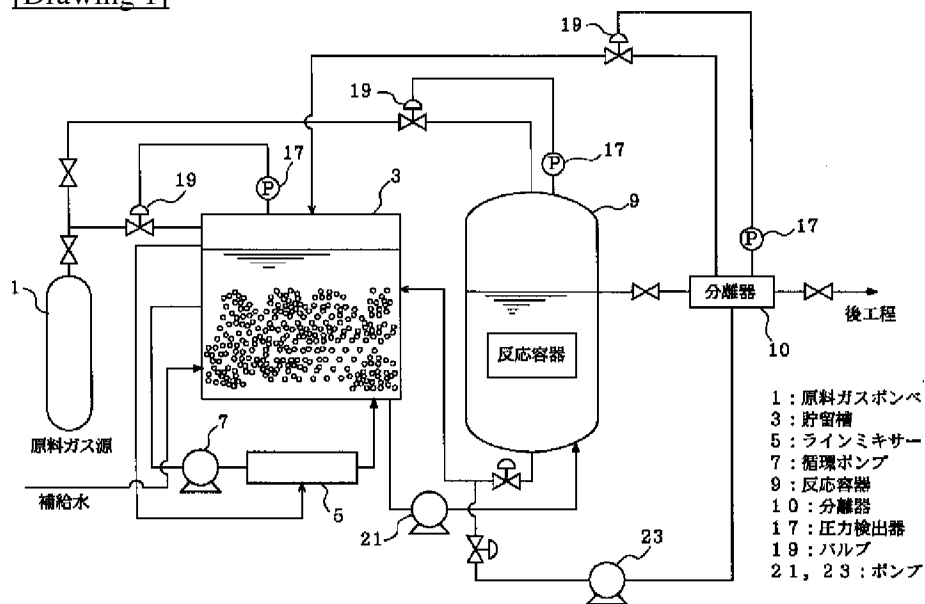
21 and 23 Pump

15 25 Coil way

27 Chiller

20 DRAWINGS

[Drawing 1]



25





[Drawing 5]

